



# PATENT SPECIFICATION

## DRAWINGS ATTACHED

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### COMPLETE SPECIFICATION

#### Improvements in or relating to processes for the Treatment of Nickelferous Ores

We, FUJI IRON & STEEL COMPANY LIMITED, a Japanese Body Corporate, of No. 10-1, 3-Chome, Marounichi, Chiyodaku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in or relating to processes for the treatment of nickelferous ores.

Nickelferous ore deposits are found in Africa, Central America, Indonesia, Japan, New Caledonia and the Philippines. The ores usually take the form of nickel-chrome iron, nickel oxide or silico-nickel ores and are known as garnierite and laterite, and various processes have been used to extract the valuable metals from them. In one known process, herein called conventional process "A", a nickel containing iron-oxide ore is ground to a powder, optionally agglomerated, the nickel present is reduced to metallic nickel by the action of a reducing gas, (an agglomerated product is crushed), then the excess iron is removed and the residual iron and nickel are simultaneously floated off. The results of this process are shown in Table I of the Tables herein, all of which are at the rear of this Complete Specification. In another known process, herein termed conventional process "B", the nickel containing iron oxide ore is reacted with FeS and coke, and the product subjected to flotation and magnetic separation. It has been reported that an ore containing 0.8—1.5% Ni, when subjected to conventional process "B", can yield a concentrate of 7—8% Ni, with a recovery of 88—95%. The final product of either process "A" or "B" can be further treated to increase the proportion of nickel present but even so, such a

treated product has disadvantages attendant to its use. Thus in the case of conventional process "A", the product has too much nickel for use in iron making while with the product of conventional process "B", the residual sulphur limits its use.

An alternative set of procedures, more commonly used for iron ores containing both nickel and chromium, is reduction roasting and subsequent magnetic separation. The results of one such a process, "C", are shown in Table II herein from which it will be seen that the bulk of the nickel present in the original ore enters the tailing. Further study of that Table will show that the use of temperatures below 1300°C with 10% of coke on garnierite crushed to a sieve size of 100 mesh cannot be expected to increase the proportion of nickel. (The mesh sizes quoted here are according to U.S.A. Tyler standard screen scale). Yet a further known process herein called conventional process "D", effects roasting at very high temperatures to convert both the nickel and iron into a ferronickel luppe. While this process effects good nickel recovery, the concentrate has a low proportion of nickel with the result that its use is difficult. The results of conventional process "D" using laterite ore are shown in Table III herein.

It should be appreciated that the separation of nickel from such ores is especially difficult since the nickel is believed to be present mainly as garnierite, with some of it in the crystal lattice of the limonite i.e., the nickel and iron ore are in intimate co-existence, and hence resistant to attempts to separate them. For example, when a limonite iron ore containing both chromium and nickel is used in a blast furnace to make iron, most of the chromium and nickel pass into the pig iron. Some nickel remains even in the steel, hindering steel production, while

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- some chromium enters the slag reducing its fluidity. All in all therefore, the purification of iron by the removal of both chromium and nickel is highly desirable, and it is an object of this invention to provide a commercially practicable method of achieving it.
- We have now discovered a process whereby the disadvantages of the aforementioned processes are minimised if not avoided completely and according to which it is possible to recover readily high grade nickel.
- This invention is based upon the realisation that nickel metal may be recovered from nickel oxide by converting the oxide to a halide salt and then roasting that to nickel powder. Obviously, these chemical reactions may be effected in one industrial step by combining the reactants.
- According to this invention, there is provided a process for the production of nickel from a nickelferous ore, in which a mixture of said ore, a halide and a reducing agent is roasted at a temperature between 700° and 1100°C.
- The nickelferous ore starting material is desirably nickel oxide or nickel-iron oxide ore, or a siliconickel iron ore.
- The ore may be treated prior to the roasting to improve the overall efficiency of the process or the purity of the product. For example, the ore may be ground — this is especially useful in the case of nickel/chrome iron ore such as laterite.
- Further, the ore may be treated to remove either or both free and combine water — laterite and garnierite each contain from 20% free water and from 10% combined water. The free water may be removed by a simple drying technique and the combined water by calcination. The conditions of calcination will vary with the ore chosen but it is currently preferred that calcination of garnierite be effected above 700°C, and calcination of laterite at above 380°C since this contains much limonite and the temperature for removing combined water from goethetite is about 360°C. Table IV illustrates the superior nickel recovery obtained by the process of this invention when the ore is pre-calcined.
- The pre-drying has certain other advantages in that it removes water which, if present, would impede heating and reduce overall yield since on evaporation, it would entrain nickel with ore dust.
- The halide to be added for the roasting is preferably an alkali-metal, ammonium or alkaline earth metal halide and is desirably provided by one or more of the following: sodium chloride, potassium bromide, calcium chloride, ammonium chloride, magnesium chloride and calcium fluoride. The halide may be added as a powder or in the form of a solution.
- The halide chosen and the concentration used both influence the amount of nickel finally recovered from the ore. Generally speaking increase in the halide content results in an increase in yield but there tends to a point beyond which increased halide concentration does not show any substantial improvement in the yield obtained. The effect of various halides on nickel recovery is shown in Table V herein, while Figure I if the accompanying drawings shows the effect of halide concentration on nickel recovery. Further, the concentration of reducing agent will tend to be related to that of the halide. For most purposes 2—6% of reducing agent is adequate, though where the ore contains an organic ingredient — as in the case of laterite — the concentration may be reduced.
- Moreover, the reducing agent, which will usually be a solid, should be of a size under 48 mesh according to the U.S. Tyler Standard screen (equivalent to a mesh of 295 micron), in order that the maximum efficiency may be obtained at all stages. The use of particles of other sizes is, of course possible, but use of greater sizes will make uniformity of dispersion difficult while smaller sizes will require greater amounts of flotation agent(s), if used.
- The reducing agent is preferably coke which may be provided by coke powder, a charcoal powder, or a wood powder. Desirably, the coke is well-mixed with the ore and halide prior to roasting.
- The ore, halide and reducing agent mixture thus formed may be either in the form of a powder or an agglomerate when water and/or binder(s) may be present.
- Roasting may be effected directly or indirectly in an atmosphere which may be reducing, neutral or slightly oxidising. The heating to 700°C should be done rapidly for the best results to be obtained and a heating velocity of more than 5°C/min is desirable. Table VI herein shows the relation between heating velocity and nickel recovery efficiency. The reason for the choice of a temperature above 700°C is that our investigations have shown that such roasting for a period in excess of 15 minutes results in the production of metallic nickel particles of such a size and nature that subsequent separation thereof is rendered easier. The roasting temperature should not exceed 1100°C since some types of ores will thereby be sintered (at least partially), slag-forming substances may fuse and metallic iron may be precipitated. The effect of roasting temperature on final nickel recovery from garnierite is shown in Figure 3 of the accompanying drawings and on laterite in Table VII herein.
- By roasting nickelferous ores in the manner just described, the metallic nickel forms precipitated particles, while most of the iron

remains as magnetite or Wustite. The precipitate is mainly pure nickel, which is susceptible to oxidation and also some cobalt, if present in the original ore.

- 5 To prevent the formation of nickel oxide(s), the roasted ore may be slightly cooled and discharged in an inert (neutral) gas, such as nitrogen; in a slightly oxidising atmosphere provided by carbon dioxide; or a slightly  
10 reducing atmosphere provided by combustion gas; or finally, in water.

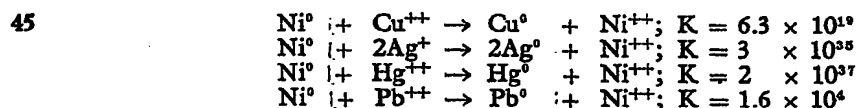
- The ore thus treated may be ground if necessary, in a non-oxidising atmosphere, then suspended and dispersed in water to provide  
15 a pulp to be subjected to flotation or magnetic separation. We prefer to concentrate the nickel in the resultant pulp by flotation and/or magnetic separation and very good yields will be obtained by the use of the techniques now specified.

- 20 If the pulp is to be subjected to flotation, because metallic nickel does not float in any

of the known flotation methods, the addition of a metallic salt or salts wherein the metal(s) has/have a lower ionization value than that of nickel is recommended, since the metal(s) precipitate(s) on the surface of the metallic nickel and functions as a flotation activator. 25

Suitable metals for the metal portion of the salt(s) include Cu, Hg, Ag; Pt, Au; Te, Sb, As, Bi, Sn and Pb. The first three are the most useful, while Pt and Au are less preferred because of their expense and the remainder because of their lower effectiveness. 30

The reaction rates of the suitable metallic salts are compared in Figures 4A and 4B of the accompanying drawings, using  $\text{Cu}^{++}$  as the sulphate,  $\text{Ag}^+$  as the nitrate,  $\text{Hg}^{++}$  as the chloride and  $\text{Pb}^{++}$  as the acetate, at an initial concentration of  $1.56 \times 10^{-4}$  mol. The equilibrium constants in substitution reactions, determined from free energy formation for each of these four metals is as follows:— 35 40



- 50 When this information is compared with the graphs of Figures 4A and 4B, it will be seen that the reaction rate increases with an increase in the value of K and, as can be seen from the graph of Figure 4B, each of the ions has a linear relationship with the  
55 square root of the nickel concentration and with time. Further study shows that  $\text{Pb}^{++}$  is the least effective activator, as foreshadowed above.

- The reaction rate is also dependent on the pulp temperature and the metal ion concentration. The dependance of the factors, in the case of  $\text{Cu}^{++}$ , is shown in Figures 5 and 6 of the accompanying drawings; Figure 5 shows the effect of temperature on an aqueous solution to which  $1.56 \times 10^{-4}$  mols of  $\text{Cu}^{++}$  (equivalent to 0.01 g) is added and Figure 6 shows the effect of  $\text{Cu}^{++}$  concentration on such a solution when maintained at 33°C. 60 65

- Accordingly, for optimum results, regard should be had to the solution temperature, the reaction time, the particular metallic salt employed and to its concentration for, as the last-mentioned increases, more nickel particles are coated but more metallic nickel is dissolved in the solution. For all these reasons, we prefer to use a pulp density of 30—40%, with the very minimum of addition of metallic salt and at a temperature  
70 75 80 above 30°C, whereby substantially complete substitution of added metal on metal nickel particles will be achieved.

A pulp thus treated, when subjected to a

flotation technique, will yield a concentrate having a high nickel content, as shown in Table IX herein. 85

In practice, it may sometimes be necessary for the roasted ore to be left for a few days prior to flotation taking place and, if this is thought to be a likely event, the pulp should be treated with either hydrogen sulphide or a water-soluble sulphide (e.g. sodium sulphide), to minimise nickel loss. Obviously this treatment may take place before or after, or even in substitution for, the reaction with the metallic salts above mentioned. Table X shows the advantages of the sulphide treatment on a pulp pretreated with the metal salts and left for some days prior to flotation. 90 95 100

Dealing now with the actual flotation itself, regard should be had to the addition of collectors and frothing agents, and to the pulp temperature and the pulp pH.

The collectors may be anionic or cationic and the following are illustrative of those substances which are suitable: xanthate, acrofloat, mercaptane, thiocarb-anibide, mercapto-benzo-thiazole, fatty acids, organic sulphonic acids and amines; suitable frothing agents are: pipe oil, camphor oil, aliphatic alcohols, ethers and phenols. Moreover, the type of collector can effect the final yield obtained — reference to Table XI herein shows the nickel recovery and the nickel content using xanthate as anion collector or an amine as cation collector. 105 110 115

So far as the flotation temperature is con-

cerned, as reference to Table XII herein shows, this is desirably at or about 50°C, although temperatures in the range of 20°—60°C may be used. So far as the pH of the pulp is concerned we prefer to use a solution having a pH between 4 and 12 and preferably exceeding a value of 5. Generally speaking, a higher nickel recovery is achieved with an acid solution while a higher nickel content in the concentrate is achieved in an alkaline solution — Table XIII herein shows the effect of solution pH on final nickel recovery.

The nickel concentrate of this invention is of great value and can be used in processes for the production of metallic nickel or of nickel alloys. It is distinguishable from the known nickel concentrates by many features, perhaps most significantly by the following:

- (a) it is of relatively high grade;
- (b) it is in the form of a powder, usually finely divided;
- (c) it is readily soluble in acid or ammonia; and
- (d) it contains a certain amount of reducing agent.

However, the concentrate thus prepared may be coated with a metal having an ionisation tendency lower than that of nickel and the product thus rendered unsuitable for the product of ferronickel.

Such additives as are present are easily removable by short period rinsing in dilute acid. Table VIII herein shows the production of ferronickel from a nickel concentrate by the use of a short rinse with 1N hydrochloric acid.

This invention extends to the pulp, the nickel concentrate and to ferronickel produced therefrom by the processes herein described.

However, the residual pulp may be treated to recover the metallic nickel therefrom and to concentrate it in any particular zone, e.g. a middling.

While the flotation technique outlined above is suitable for the recovery of nickel from most nickelferous ores, we also prefer to use magnetic separation for the treatment of roasted garnierite low in iron.

In the case of nickel-chromium iron ores especially — but not exclusively — the roasted ore optionally crushed is subjected to magnetic separation.

The conditions of magnetic separation will vary with the conditions of roasting of the ore, the amplitude of the magnetic field applied and the size of the roasted ore. While it is not absolutely necessary to crush the roasted ore prior to magnetic separation, we prefer to do so, because of the better results obtained. Tables XIV and XV herein

show the results obtained using garnierite roasted according to the invention, and Table XV especially shows the effect of pre-separation crushing. Generally speaking, use of a higher magnetic field effects higher nickel recovery but a low proportion thereof in the concentrate and *vice versa*.

No specific indication can be given for the magnetic separation of any particular roasted ore, but we have found that a cycle of magnetic field application and crushing gives overall efficiency for most roasted ores.

Of course, it is possible to roast an ore by a process according to this invention and then subject it to consecutive flotation or magnetic separation in that or the reverse order. Similarly, it is possible to apply either treatment selectively, either to a concentrate or a tailing.

In a preferred procedure, the flotation technique may be used to recover metallic nickel from the roasted ore which comprises a portion of metallic nickel deposited on the reducing agent and some gangue, and a portion of fine powder nickel within the gangue. The nickel in the tailing may be economically recovered by the use of finely dividing, and repeated flotations.

In a further preferred procedure, the tailing obtained by flotation is separated by magnetic separation and the concentrate obtained is either directly used as a low grade nickel concentrate or further refined by repeated flotation or magnetic separation to yield a high grade nickel concentrate. The use of this latter process and the results obtained is shown in Table XVI herein from which it can be seen that some 45% of nickel present in the tailing can be recovered by subjecting it to magnetic separation.

Certain ores may require specialised treatment. Thus an iron oxide ore containing a little nickel and a little chromium should, after roasting, be subjected to magnetic separation which will provide an iron and nickel concentrate, non-magnetic chromite and gangue. Thereafter only the iron and nickel concentrate should be subjected to flotation. Such a procedure provides a valuable by-product, a low grade iron ore rich in chromium.

This invention extends to the nickel whenever prepared in or by the flotation and/or magnetic separation techniques aforementioned, and to the by-products, including a low grade iron ore rich in chromium.

In order that this invention may be well understood, Examples will now be given to show, though by way of illustration only, the processes herein described.

#### EXAMPLE 1:

Iron oxide ore containing nickel from Omonhon in the Philippines, and as a powder of particles under 38 $\mu$ , the overflow from

cyclone classification was mixed with 3% powdered coke under 48 mesh and 2.5%  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and the mixture roasted at 970°C for one hour. Water was added to give a slurry of 35% pulp concentration, and 1.5 kg per ton of the roasted ore of cupric sulphate was added to the slurry maintained at 60°C, which was then stirred for 20 minutes. The slurry was transferred to a flotation machine to provide a 10% slurry maintained at 40°C, to which 500 g. per ton of sodium sulphide was added and the mixture stirred for five minutes. Sul-

phuric acid was added to the slurry to bring its pH to 6, and then 500 g. per ton of potassium isoamylxanthate and one drop of pine oil were added and flotation was effected for five minutes.

300 g. per ton of potassium iso-amyl-xanthate was added to the tailing, which was subjected to flotation for three minutes. The nickel rougher concentrate and scavenger concentrate thus obtained were collected and subjected to cleaner flotation. The following results were obtained:—

	Weight %	Ni %	Ni recovery
Raw Ore		0.99	
Roasted Ore	100.0	1.13	
Cleaner Concentrate	6.2	15.83	86.3
Cleaner Tailing	11.2	0.32	
Scavenger Tailing	82.6	0.14	

#### EXAMPLE 2:

Nickeliferous iron oxide ore (containing 0.8% Ni) from Miyakawa, Japan, was crushed to under 60 mesh and dried by heating. The powdered ore thus prepared was mixed with 2.8% powdered coke (under 48 mesh size), 5% sodium chloride, and 5.3% calcium chloride. The mixture was heated to 1050°C in a roasting furnace at a heating rate of 10°C/min., held at that temperature for an hour and then cooled to about 300°C in a stream of nitrogen. It was then put in water, slightly crushed by a wet-type crusher, and treated by a thickener to provide a 40% concentrated pulp. This pulp was maintained at 60°C and stirred for five minutes with addition of 1.6 kg/t of silver nitrate, and then diluted to 20% concentrated pulp. This pulp was subjected to flotation at a temperature of 45°C with addition of 500 g/t of potassium iso-amyl-xanthate and small amount of pine oil.

The rougher tailing was subjected to scavenger flotation with addition of 250 g/t of xanthate and rougher concentrate and scavenger concentrate were collected and subjected to cleaner flotation. In this way, a

cleaner concentrate containing 8.8% Ni was obtained (nickel recovery of 83.1%).

#### EXAMPLE 3:

Silico magnesia nickel ore from New Caledonia was crushed to under 65 mesh sieve size and calcined at 750°C. The calcined ore was well mixed with 3.5% powdered coke under 48 mesh size, 10% ammonium chloride with a small volume of water and then pelletized. The pelletized ore was heated to 900°C in a roasting furnace at a heating rate of 10°C/min., maintained at that temperature for one hour and then cooled to the room temperature in a stream of nitrogen. The product was slightly crushed (to under 65 mesh size) in water, and maintained at 50°C and stirred for 15 minutes with addition of 1.2kg/t of mercuric chloride. The resultant slime was sulphurated by passing hydrogen sulphide there-through for 2 minutes, and then lime was added thereon to adjust the pH to 10. The slime was subjected to flotation for 8 minutes with addition of 250g/t of roasted ore of Aerofloat, 250g of potassium iso-amyl-xanthate, and a small amount of pine oil.

The following results were obtained:—

	Weight %	Ni %	Ni Distribution
Raw Ore		2.89	
Roasted Ore	100	3.25	
Concentrate	10.8	19.61	80.3
Tailing	89.2	0.52	19.7

**EXAMPLE 4:**

5 Silico magnesia nickel ore of from New Caledonia was crushed to under 65 mesh sieve size, mixed with 4% of powdered coke under 48 mesh size, and 4% of anhydrous calcium chloride. The mixture was then heated to 950°C at a heating rate of 10°C/min. and kept that temperature for one hour. The roasted ore was crushed to under 150 mesh size by a wet process to a 35% concentrated pulp and which was then stirred for 20 minutes with addition of 1.5kg/t of cupric sulphate at 60°C. The resultant slime was transferred to a flotation machine to

provide a 10% concentrated pulp maintained at 40°C, which was then stirred for 5 minutes with addition of 500 g/t of sodium sulphide. The pulp pH was adjusted to 6 by the use of sulphuric acid, and the pulp then subjected to rougher flotation for 5 minutes, with addition of 500 g/t of potassium iso-amyl-xanthate and one drop of pine oil. The rougher tailing was subjected to scavenger flotation for 3 minutes with addition of 300g/t potassium iso-amyl-xanthate. The rougher and scavenger nickel concentrate was collected and subjected to cleaner flotation and the following results obtained:—

	Weight %	Ni %	Ni Yield %
Raw Ore		3.98	
Roasted Ore	100.0	4.05	
Cleaner Concentrate	13.1	26.75	86.7
Cleaner Tailing	14.2	0.75	
Scavenger Tailing	72.7	0.59	

**EXAMPLE 5:**

35 Garnierite ore from New Caledonia (and composed of 2.89% Ni; 12.02% Fe, 24.34% MgO, 40.80% SiO<sub>2</sub>, 0.11% Co, 0.71% Cr, 0.31% MnO, 0.10% CaO, 0.75% Al<sub>2</sub>O<sub>3</sub> and 11.63% (C.W.) was crushed to under 65 mesh, and mixed with 3.5% powdered coke

(of under 48 mesh size) and 7% anhydrous calcium chloride. The mixture was roasted at 1050°C for one hour, then crushed to under 150 mesh size and separated by a wet type magnetic separator (Sala type) at 1000 Gauss. The following results were obtained:—

		Concentrate	Tailing
Amount Produced %		7.65	92.35
Ni %		30.80	0.52
Ni Recovery %		83.10	16.90
Other Elements	C %	1.44	1.80
	Fe %	55.80	7.63
	S %	0.07	
	MgO %	3.09	
	SiO <sub>2</sub> %	5.83	

EXAMPLE 6: Nickel concentrates from various sources were analysed and found to have the following compositions:—

Source of Ore	Ni (Original in Ore)	Fe (Original in Ore)	Co	C	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO
Laterite (Omonhon)	15.83 (0.84)	50.20 (43.85)	0.45	9.75	3.81	6.93	
Laterite (Omonhon)	22.35 (0.99)	44.45 (49.25)	0.78	4.81			
Laterite (Wakasa)	4.24 (0.43)	14.63 (47.05)	0.27	65.95			
Laterite (Miyakawa)	8.80 (0.84)	28.87 (47.17)	0.23	41.28			
Garnierite	19.35 (2.89)	26.05 (12.02)		18.02	16.18		9.92
Garnierite	28.55 (2.89)	22.95 (12.02)		7.53	19.42		10.97
Garnierite	37.10 (2.89)	27.20 (12.02)		9.77	12.08		6.70

## SCHEDULE OF TABLES REFERRED TO IN THE FOREGOING DESCRIPTION

TABLE I

Results of operating conventional process "A"

	Weight (g)	Total Nickel	Metallic Nickel	Total Iron	Metallic Iron
Raw Ore	200	1.05	—	35.5	—
Roasted Ore	192	—	0.89	—	14.2
Metallic Iron	30	—	0.50	—	86.0
Mixture of Metallic Iron and Nickel	6.4	—	23.80	—	40.5
Tailing	143	—	0.08	—	0.05

TABLE II

Use of conventional process "C" on garnierite  
100% ground ore of 100 mesh, magnetic separation  
being effected by a SALA drum wet type

Reduction Conditions			Ore Composition	
Temperature °C.	Time hr.	Coke %	Fe <sub>2</sub> O <sub>3</sub> %	NiO %
1200	10	10	12.02	2.89
1250	8	10	12.02	2.89
1300	8	10	12.02	2.89

Concentrate			Tailing		
Yield	Ni %	Ni % Recovery	Yield	Ni %	Ni % Recovery
7.4	2.65	6.83	92.6	2.27	93.17
5.9	2.784	7.11	94.1	2.15	92.89
3.6	2.75	4.05	96.4	2.11	95.95



TABLE III

Use of conventional process "D" on laterite

Magnetic Separation  
Yield Weight %

Source of Ore	Concentrate	Tailing
Omonhon Overflow	74.8	25.2
Wakasa Overflow	69.7	30.3
Miyakawa Overflow	65.2	34.8

Chemical Composition of Concentrate %

Source of Ore	Total Fe	Cr	Ni	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P	S
Omonhon Overflow	88.62	0.46	1.79	2.99	1.50	0.44	0.014
Wakasa Overflow	89.34	0.36	0.89	2.99	2.04	0.019	0.007
Miyakawa Overflow	89.43	0.40	1.62	1.23	3.14	0.016	0.004

Chemical Composition of Tailing %

Source of Ore	Total Fe	Cr	Ni	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
Omonhon Overflow	41.49	3.05	0.03	13.12	10.82
Wakasa Overflow	28.16	3.88	0.08	20.37	24.12
Miyakawa Overflow	28.64	2.41	0.06	9.35	33.90

Recovery in  
Concentrate %Removal Rate  
into Tailing %

Source of Ore	Fe	Ni	Cr	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
Omonhon Overflow	86.4	99.3	69.4	59.6	70.9
Wakasa Overflow	87.9	96.7	82.5	74.8	83.7
Miyakawa Overflow	85.4	98.1	76.4	80.2	85.3

TABLE IV

Effect of the calcination on nickel recovery

Ore Type	Roasting Conditions	Nickel content in (concentrate) %	Nickel recovery (net) %
Laterite	non-calcined	7.55	77.6
	calcined at 700° C.	8.80	83.1
Garnierite	non-calcined	16.60	77.8
	calcined at 750° C.	19.35	86.9

TABLE V

Effect of type of halide on final nickel recovery  
(using 3.5% by weight of coke, all parts % by weight)

Halide(s)	Amount added (%)	Roasting Temperature (°C.)	Nickel %	Nickel Recovery
CaCl <sub>2</sub>	10	950	19.4	87.0
NH <sub>4</sub> Cl	10	950	19.6	80.3
MgCl <sub>2</sub>	17	950	21.2	54.8
NaCl	10.6	1050	11.8	70.5
NaCl + CaCl <sub>2</sub>	10.6	1050	15.0	72.9
NH <sub>4</sub> Cl + CaF <sub>2</sub>	8.5	950	18.5	36.8
CaF <sub>2</sub>	7.4	950	5.0	30.0
KBr	10.3	950	9.2	21.5

TABLE VI

Effect of heating velocity on final nickel recovery,  
using garnierite ore

Heating Velocity °C./minute	Ni % Concentrate	Ni Recovery %
10	21.3	73.2
5	22.5	64.0

TABLE VII

Effect of roasting temperature on final nickel recovery, using laterite of Omonhon ore, non-calcined, but with 4%  $\text{CaCl}_2$  and 2% coke

Roasting Temperature °C.	Concentrate Ni %	Tailing Ni %	Recovery Ni %
900	11.1	0.62	36.2
950	22.1	0.27	65.3
1000	13.7	0.33	65.5

TABLE VIII

Treatment of concentrate with acid, and analysis of the product

Treatment of Concentrate/ Analysis in %	Flotation Nickel Concentrate	Copper Removed Concentrate	Ferronickel Produced
Ni	25.35	25.80	48.18
C	18.02	19.10	0.84
Total Fe	26.05	28.44	49.06
MgO	7.92	6.23	
$\text{SiO}_2$	10.68	8.50	
Cu	1.10	0.05	0.05
S	0.48	0.12	0.01

TABLE IX

Effect of addition of metallic salts on final nickel recovery, using garnierite ore

Metal Salt		Flotation Results	
Type	Amount/kg/ton	Ni Content (Concentrate) in %	Ni Yield (%)
Nil	—	7.12	10.2
$\text{CuSO}_4$	1.5	26.75	86.7
$\text{AgNO}_3$	1.8	21.00	70.2
$\text{HgCl}_2$	1.2	20.90	74.6

TABLE X

Effect of sulphuration on final nickel recovery

Reaction	Concentrate Ni %	Yield Ni %	Flotation
No $\text{Na}_2\text{S}$	19.0	86.3	} immediately after roasting
$\text{Na}_2\text{S}$ added	19.3	86.9	
No $\text{Na}_2\text{S}$	26.4	64.1	} several days after roasting
$\text{Na}_2\text{S}$ added	14.7	84.2	

TABLE XI

Effect of collector on efficiency of nickel recovery,  
conditions:  $\text{CaCl}_2$  7%; Coke 3.5%, roasted at  $950^\circ\text{C}$ ., floated at  $43^\circ\text{C}$ .,  $\text{pH} = 5.6$

Collectors type	Ni Content (Concentrate) %	Ni Recovery %
Anionic (potassium iso-amyl- xanthate)	19.9	72.5
Cationic (dodecylamine)	25.0	70.2

TABLE XII

Effect of flotation temperature on final nickel

Temperature ( $^\circ\text{C}$ .)	Ni Content (Concentrate) %	Ni Recovery %	Remarks
40	30.5	80.4	10% $\text{CaCl}_2$
50	26.7	85.0	1.8% Coke
60	20.0	80.8	

TABLE XIII

Effect of solution pH on final nickel recovery ore roasted at 950° C.  
with varying amount of halides and solid reducing agents

Test No.	at pH 5 — 6		at pH 10 — 12	
	Ni % (Concentrate)	Ni Recovery %	Ni % (Concentrate)	Ni Recovery %
1	15.9	79.3	17.0	72.5
2	28.6	84.8	37.1	80.9
3	16.5	86.7	24.2	81.3
4	18.5	85.8	24.9	75.7
5	16.5	77.8	19.5	66.0

TABLE XIV

Effect of magnetic separation on roasted garnierite

Roasting Temperature °C.	Magnetic Field (Gauss)	Ni % in (Concentrate)	Ni % in Tailing	Ni Recovery %	Roasted ore size
800	1000	23.70	1.81	38.5	crushed
930	1000	31.30	0.70	77.0	crushed to under 150 mesh
1050	1000	30.80	0.52	83.1	crushed to under 150 mesh
950	5000	4.67	0.55	88.9	not crushed (under 60 mesh)
1000	5000	6.42	0.34	92.8	not crushed (under 60 mesh)
1050	2800	11.50	0.36	90.0	not crushed (under 60 mesh)

TABLE XV

Effect of crushing prior to magnetic separation

	Not Crushed		Crushed to under 150 mesh	
	Concentrate	Tailing	Concentrate	Tailing
Yield Wt. %	21.9	78.1	7.65	92.35
Ni %	11.50	0.36	30.80	0.52
Ni Recovery	90.0	10.0	83.10	16.90
Cr %	6.87	0.52	1.44	1.80
Cr Recovery	78.8	21.2	6.2	93.8
Total Fe %	25.38	7.42	55.80	7.63
Total Fe Recovery	48.9	51.5	37.7	62.3
Magnitude of Magnetic Field	2800 gauss		1000 gauss	

TABLE XVI

The use of combined flotation and magnetic separation of roasted garnierite

Source	Amount Produced	Nickel %	Nickel Distribution %	Remarks
Flotation Concentration	8.75	25.30	71.80	
Middling	11.50	2.27	8.43	
Tailing	79.72	0.76	19.77	
Magnetic Separation Concentration	6.40	4.29	8.84	} Flotation tailing is used
Tailing	73.32	0.37	10.93	

## WHAT WE CLAIM IS:—

1. A process for the treatment of nickeliferous ore, in which a mixture of said ore, a halide and a reducing agent is roasted at a temperature between 700°C and 1100°C.
2. A process as claimed in claim 1, in which said metallic nickel is recovered by flotation.
3. A process as claimed in claim 2, in which said roasted ore is optionally ground, with or without water, and a metallic salt or salts of a metal or metals having a lower ionization value than that of nickel added, prior to flotation.

4. A process as claimed in any of the preceding claims, in which said metallic nickel is recovered by magnetic separation.

5. A process as claimed in claim 4, in which said roasted ore is crushed prior to magnetic separation.

6. A process as claimed in any of the preceding claims, in which said nickeliferous ore is selected from those exemplified herein.

7. A process as claimed in any of the preceding claims, in which said ore is dried and/or calcined and/or crushed prior to the roasting.

8. A process as claimed in any of the

- preceding claims, in which heating to the roasting temperature is effected at a rate of more than 5°C/min.
- 5 9. A process as claimed in any of the preceding claims, in which the roasting period is in excess of 15 minutes.
10. A process as claimed in any of the preceding claims in which said reducing agent is a solid.
- 10 11. A process as claimed in claim 10, in which said reducing agent is of particles the size of which is under 48 mesh according to the U.S. Tyler Standard screen size.
- 15 12. A process as claimed in either of claims 10 and 11, in which said reducing agent is present in a concentration of from 2—6% by weight of the ore.
- 20 13. A process as claimed in any of claims 10 to 12, in which said reducing agent is coke, charcoal or wood powder.
14. A process as claimed in any of the preceding claims, in which said halide is an alkali metal, ammonium or alkaline earth metal halide.
- 25 15. A process as claimed in claim 14, in which the halide is selected from those exemplified herein.
- 30 16. A process as claimed in any of the preceding claims, in which the roasted product is cooled and discharged into a non-oxidising atmosphere to prevent oxidation of the nickel.
17. A process as claimed in any of the preceding claims, in which the product is subjected to a short rinse in dilute acid to produce ferronickel.
- 35 18. A process as claimed in claim 3, in which said metallic salt or salts is a salt or salts of copper, mercury or silver.
- 40 19. A process as claimed in claim 3 or 18, in which addition of said metallic salt(s) is effected at a temperature above 30°C.
20. A process as claimed in claim 3, 18 or 19, in which the pulp density is from
- 45 30—40%.
21. A process as claimed in claim 3 or any of claims 18 to 20, in which the concentrate is treated with hydrogen sulphide or a water-soluble sulphide.
22. A process as claimed in claim 3 or any of claims 18 to 21, in which flotation is effected in the presence of a collector or collectors.
23. A process as claimed in claim 3 or any of claims 18 to 22, in which flotation is effected in the presence of a frothing agent or agents.
24. A process as claimed in claim 3 or any of claims 18 to 23 in which flotation is effected at a pH of between 4 and 12.
25. A process as claimed in claim 24, in which flotation is effected at a pH exceeding a value of 5.
26. A process as claimed in any of claims 3 or 18 to 25, in which flotation is effected at a temperature between 20° and 60°C.
27. A process as claimed in any of the preceding claims, substantially as herein described.
28. A process for the treatment of nickel-ferrous ores substantially as herein described with reference to any of the Examples.
29. A process for the treatment of nickel-ferrous ore substantially as herein described with reference to any of the accompanying drawings.
30. Nickel concentrate whenever prepared in or by a process as claimed in any of the preceding process claims.
31. Nickel whenever prepared in or by a process as claimed in any of the preceding process claims.
32. Ferronickel whenever prepared in or by a process as claimed in any of the preceding process claims.
33. By-products whenever prepared in or by a process as claimed in any of the preceding process claims.
34. A low grade iron ore rich in chromium whenever prepared in or by a process as claimed in any of the preceding process claims.

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FIG. 1.

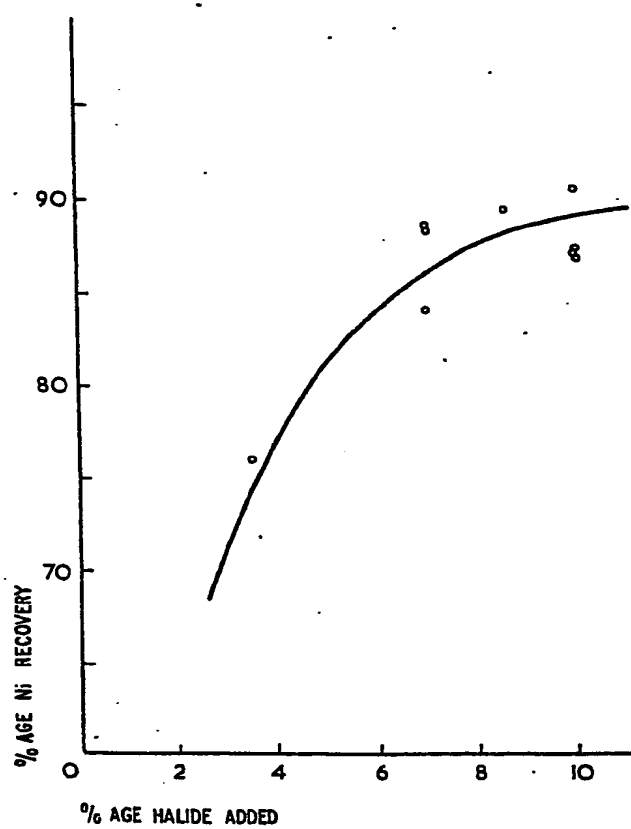




FIG. 2.

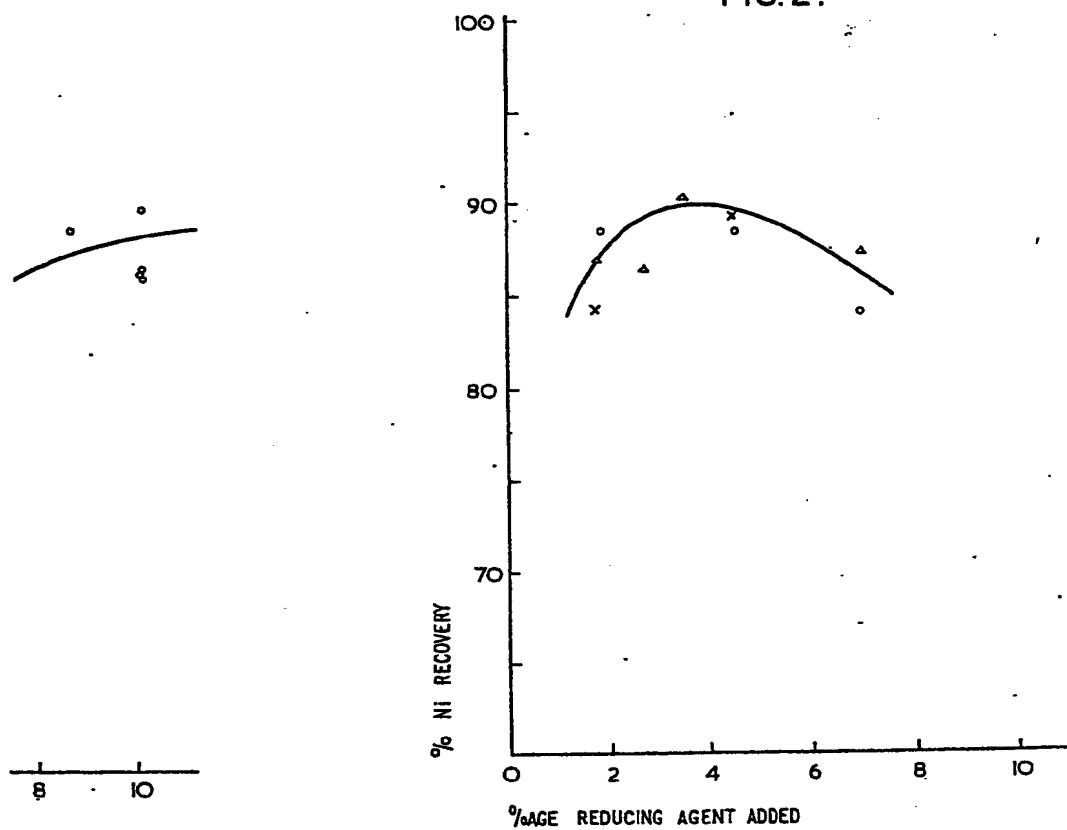


FIG. 1.

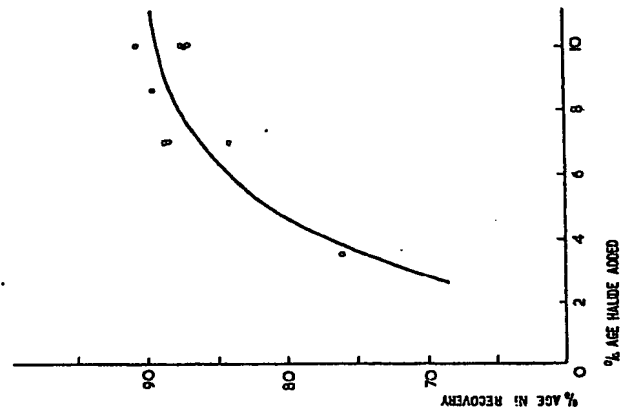


FIG. 2.

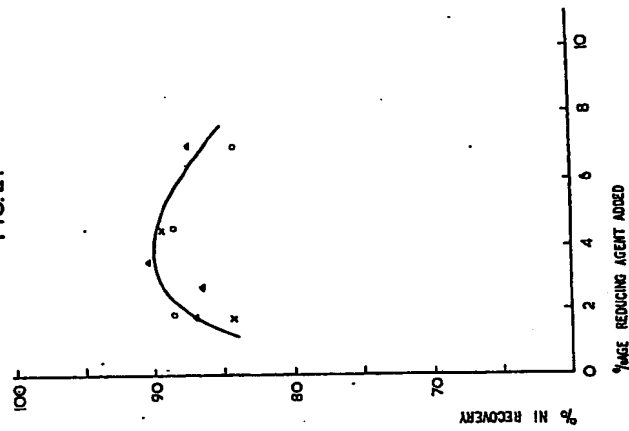
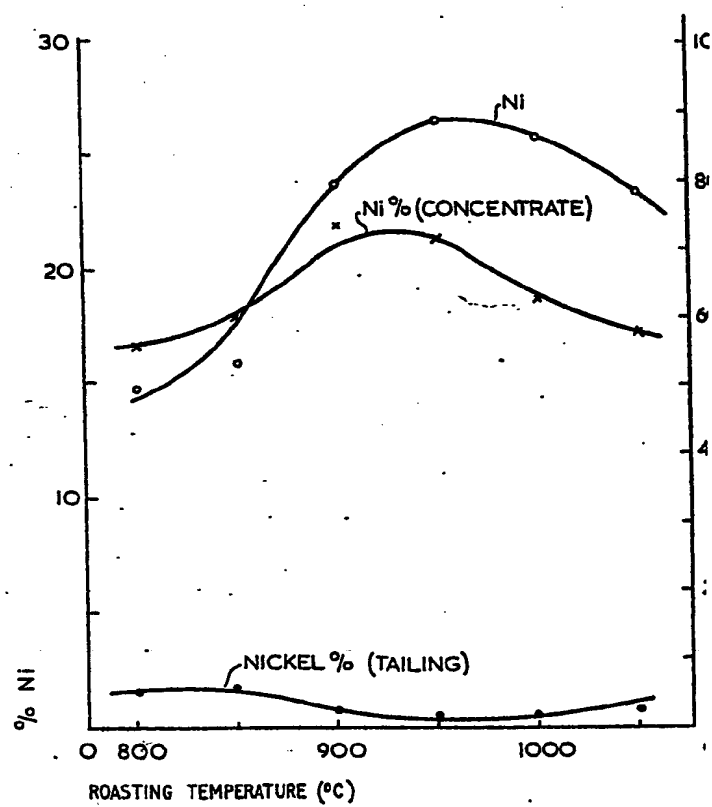


FIG.3.



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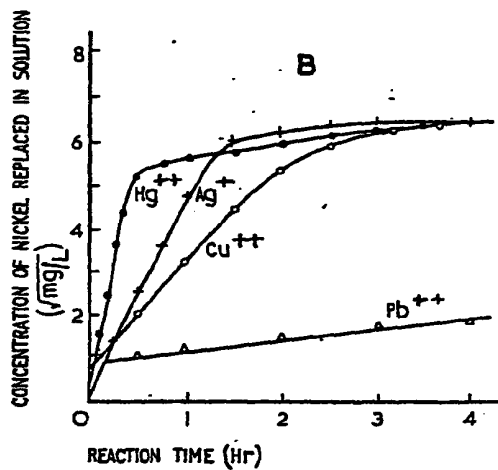
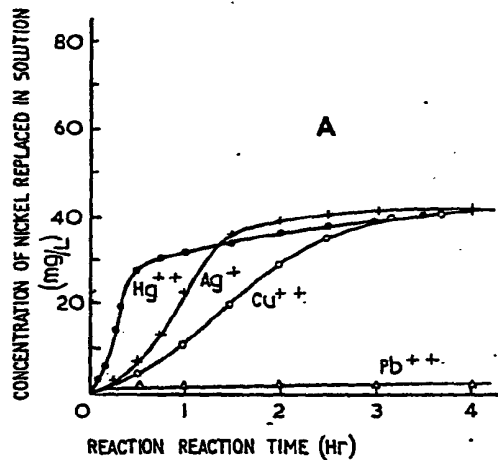
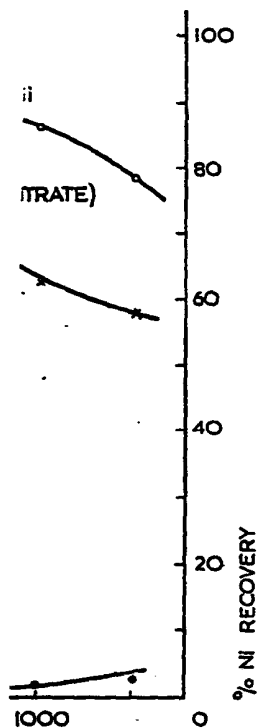
COMPLETE SPECIFICATION

6 SHEETS

This drawing is a reproduction of  
the Original on a reduced scale

Sheets 3 & 4

FIG. 4.



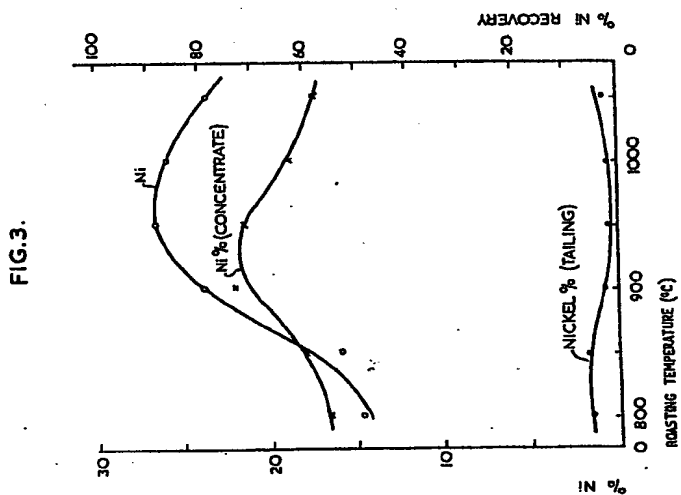


FIG. 4.

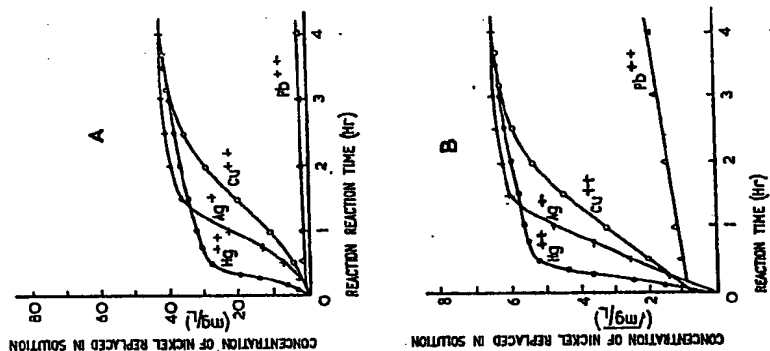


FIG. 5.

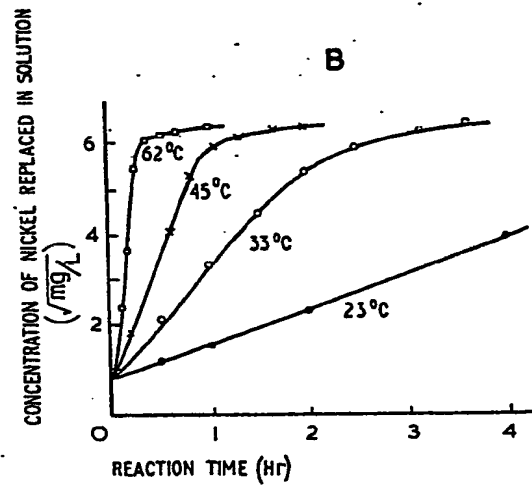
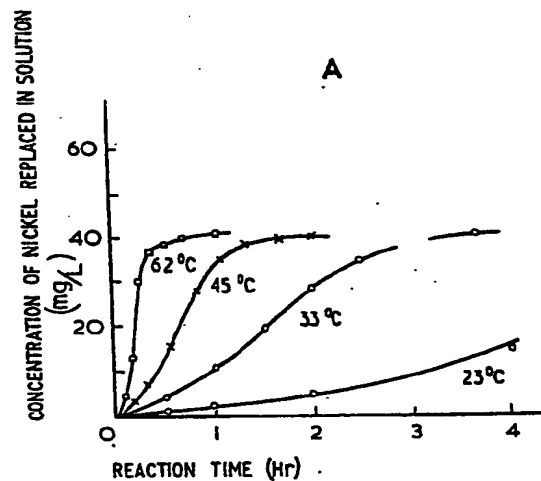


FIG. 6.

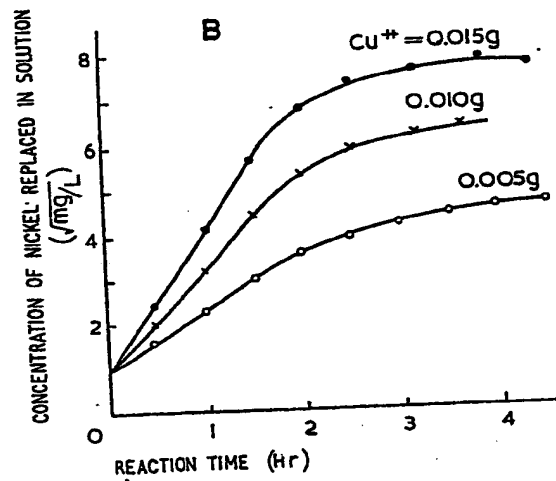
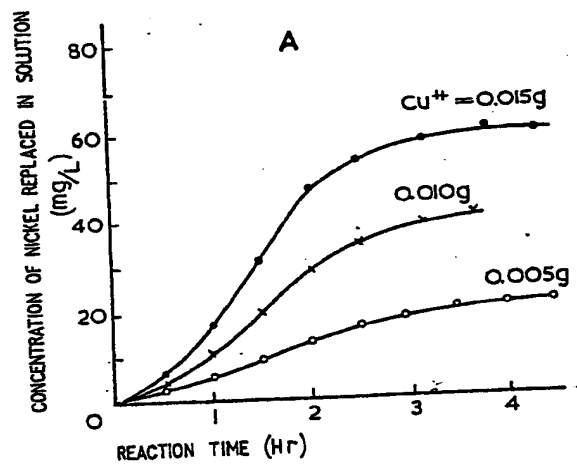


FIG. 6.

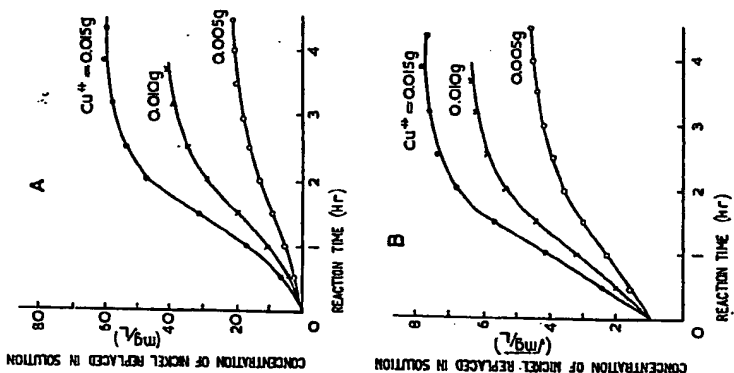


FIG. 5.

